Non conventional screening of the Coulomb interaction in low dimensional and finite size system

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We study the screening of the Coulomb interaction in non polar systems by polarizable atoms. We show that in low dimensions and small finite size systems this screening deviates strongly from that conventionally assumed. In fact in one dimension the short range interaction is strongly screened and the long range interaction is anti-screened thereby strongly reducing the gradient of the Coulomb interaction and therefore the correlation effects. We argue that this effect explains the success of mean field single particle theories for large molecules.

In model Hamiltonians such as the Hubbard model set up to treat correlation effects the on-site Coulomb interaction is a very important parameter. It is usually argued that this interaction is only weakly screened relative to the longer range interactions which justifies the neglect of the later [1]. In order to decide on the importance of the correlation effects precise knowledge of the longer range Coulomb interactions is crucial since of course it is the gradient of this interaction which really matters. In the last years for instance correlation effects have been an important topic in the debate on high T_c superconductors, colossal magneto resistance materials, Kondo and heavy fermion systems, organic conductors and (doped) fullerenes. Usually one uses dielectric response theory to estimate the range of the Coulomb interaction and one comes to the conclusion that the effective interaction is very short range without really asking whether or not this theory is applicable. In this paper we study the static dielectric response of a non polar insulator to the Coulomb potential generated by two electrons and show that the above mentioned approximation is very incorrect leading not only to quantitatively but also qualitatively different physics. We show that the well known Clausius-Mossotti (C-M) theory of dielectrics which is valid for large distances in 3 dimensions breaks down at short distances and for lower dimensions in general. At very short distances between two electrons the Coulomb potential is a rapidly varying function of distance so that the local field corrections have to be taken into account. We show that on one and two dimensional systems (lines and planes of atoms) and large molecules the screening of the (3 dimensional) Coulomb field is totally due to local field corrections. For finite systems, like molecules, the effective

Coulomb interaction deviates strongly from the $(\epsilon r)^{-1}$ like behavior assumed in dielectric response theory. The dependence on distance turns out to be much weaker giving rise to a more uniform potential for the electrons. In fact in low dimensions the situation is quite the opposite to that usually assumed in that the short range interactions are efficiently screened whilst the longer range interactions are anti-screened. This results in a drastic reduction of correlation effects, providing a rational for the success of one electron mean field like theories to describe the electronic structure of organic molecules.

We consider our systems to be composed of polarizable atoms. If we assume a linear response of the atoms to an electric field, the induced dipole moment $\mathbf{p}(\mathbf{r}_i)$ on an atom on site $\mathbf{r}_i$ is proportional to the local field $\mathbf{F}(\mathbf{r}_i)$: $\mathbf{p}(\mathbf{r}_i) = \alpha_i \mathbf{F}(\mathbf{r}_i)$, where α is the atomic polarizability. Assuming the electric field is constant over the size of the atom, the energy of the system is lowered due to the induced dipole moment by an amount of $\Delta E_i = -\frac{1}{2}\alpha_i |\mathbf{F}(\mathbf{r}_i)|^2$. Using this, the screening energy of the Coulomb interaction of two electrons on the same lattice point (the Hubbard U) can be obtained [2].

Clausius and Mossotti derived the relation between the microscopic polarizability and the macroscopic dielectric constant $\frac{\epsilon-1}{\epsilon+2} = 4\pi\alpha/3$, assuming that the external potential can be considered as being uniform in a region around each atom, and that one can treat this region as a continuum. If the electrons are close to each other, one has to take into account that a lattice consists of a discrete set of atoms. We show below that this has important consequences if the distance between the electrons is of the order of the lattice spacing or if the dimensionality of the system is low.

The mathematical description of the microscopic response of a system of point-dipoles to external fields was developed by Mott and Littleton [3] and has proven to be a powerful method to calculate for instance local field corrections for point-charge defects [4] and (surface) core-level shifts in photoemission [5,6]. Consider two electrons, one at the origin of our coordinate system and one at $\mathbf{R}$. The aim is to calculate the electrostatic energy V of the system as a function of $\mathbf{R}$. The total energy consists of four parts: the potential energy due to the monopole-monopole, monopole-dipole and dipole-dipole interactions plus the energy stored in the induced dipoles [4]. The total electrostatic energy is given by:

$$V(\mathbf{R}) = \frac{e^2}{R} - \frac{1}{2}\sum_i \mathbf{d}_i \cdot \mathbf{p}_i \equiv \frac{e^2}{R} - 2E_p(\mathbf{R}), \qquad (1)$$

where $\mathbf{d}_i$ is the total external monopole field and $\mathbf{p}_i$ the induced dipole moment at site i. The bare Coulomb repulsion is reduced by the polarization energy $2E_p(\mathbf{R})$, as defined in the last part of equation (1). Now the dipole moment at each site has to be determined. The induced dipole moment is proportional to the local field on the atom, leading to:

$$\mathbf{p}(\mathbf{r}) = \alpha e\mathbf{r}/|r|^3 + \alpha e(\mathbf{r} - \mathbf{R})/|r - R|^3$$
$$+ \alpha \sum_{\mathbf{l},\mathbf{l}\neq 0} \frac{1}{|l|^5} \{ [3\mathbf{p}(\mathbf{r}+\mathbf{l}) \cdot \mathbf{l}] \, \mathbf{l} - |l|^2 \mathbf{p}(\mathbf{r}+\mathbf{l})\}. \quad (2)$$

This equality for N atoms results in DN coupled equations for $\mathbf{p}(\mathbf{r}_i)$, where D is the dimensionality of the system. If the symmetries of the problem are taken into account, the number of equations that actually have to be solved can be substantially reduced. The matrix representation of equation (2) in Cartesian coordinates is:

$$p_i^\mu = \alpha_i d_i^\mu + \sum_\gamma \sum_{j, j\neq i} M_{ij}^{\mu\gamma} p_j^\gamma, \text{ with } \mu, \gamma = x, y, z. \quad (3)$$

The elements of the matrix that represents the dipole-dipole interactions are given by:

$$M_{ij}^{\mu\gamma} = \alpha_i(3l_{ij}^\mu \, l_{ij}^\gamma \, |l_{ij}|^{-5} - |l_{ij}|^{-3} \, \delta_{\mu\gamma}), \qquad (4)$$

where $\mathbf{l}_{ij} = \mathbf{l}_i - \mathbf{l}_j$ is the vector connecting the two dipoles. The solution of this set of equations gives the exact effective potential for the electrons. In some cases the equation can be solved in wave-vector space [7], but in general the less cumbersome method is to solve the equation numerically in real space.

The formulation above reduces to the C.-M. relation when a) the dipole-dipole interaction is averaged over and b) the lattice is treated as a continuum. This is easily shown as from the C.-M. relation follows that $\mathbf{p}_i = \alpha_i \frac{\epsilon+2}{3\epsilon}\mathbf{d}_i$ so that $2E^p(\mathbf{R}) = \frac{\epsilon+2}{3\epsilon} \frac{4\pi\alpha e^2}{R}$ and the well know result $V(\mathbf{R}) = e^2/\epsilon R$ is obtained if the summation over the lattice vectors is replaced by an integration. An obvious improvement up on the C.-M. result is to evaluate the lattice sum in equation (1) exactly. Within this partial continuum limit of this model, where dipole-dipole interactions are taken into account on the Clausius-Mossotti level, values for the polarization energy and the effective on-site Coulomb interaction U that compare well with experiment can be obtained [8].

If one wants to take the dipole-dipole interaction into account without using the Clausius-Mossotti relation, one has to solve the matrix equation (3). Only a limited number of equations can be solved numerically, typically a few thousand. For a 3D cubic system the exact effective potential deviates not more than around 10% from the

C.-M. expression, except if the charges are at the same site, as has been discussed before [2].

The situation is very different for a system where the dipoles and electrons are confined to a plane (2D system) or a line (1D system), a geometry that can be encountered in a material where a chain of polarizable atoms is embedded in a non polarizing matrix. As the system is an object in the 3D real space, the bare Coulomb interaction between the two electrons is inversely proportional to the distance between the charges. For a 1D system the polarization energy is calculated exactly and shown in figure 1. At very short distances (till about 2 lattice spacings) the Coulomb interaction is screened. When the separation between the charges is larger, however, the Coulomb interaction is *anti-screened*: the induced polarization results in an increased repulsion between the two charges. This behavior is markedly different from the C.-M. result. In fact it is the opposite to the usually assumed behavior that long range interactions are screened and short range interactions not or weakly.
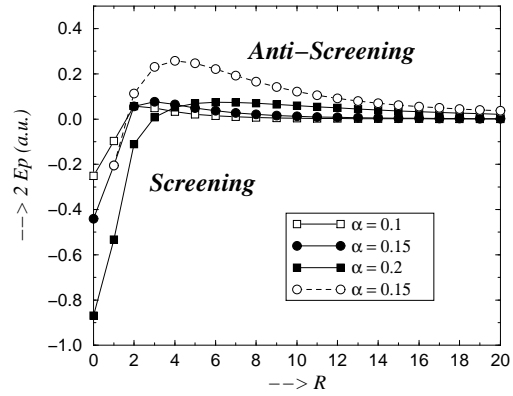

FIG. 1. The polarization energy $2E_p$ as a function of separation between the electrons in one dimension. The lattice spacing is taken to be unity. The dashed line represents $2RE_p$ for $\alpha = 0.15$. Negative values of E_p represent screening and positive values anti-screening.

In the figure also RE_p as a function of distance is shown. If a dielectric constant ϵ can be defined then $2RE_p = 1 - 1/\epsilon$. From the figure it can be seen that $2RE_p \to 0$ when $R \to \infty$, so that at large distances $\epsilon \to 1$ and the Coulomb potential is unscreened. As a consequence the effective potential between the charges is flattened out. At short distances the bare Coulomb potential is large, but also the polarization energy is large, see figure 2. At intermediate distances the Coulomb potential decays, but the polarization enhances the repulsive interaction so that in the end the effective potential decays much slower than $1/R$. In a two dimensional system an analogue situation is encountered. At short distances local fields screen the potential and at large distances the potential is again unscreened.

Why is this result so different from what one expects on the basis of the C.-M. relation? If the distance between the electrons is large the lattice can be treated as a continuum. and the lattice sum can be replaced by an integral. In the low dimensional systems the outcome of the integral does not only depend on the distance between the two electrons, but also on the range of integration. In order to make the integral convergent we have to assume a sphere around each electron with radius r_0, in which the polarizability is zero.
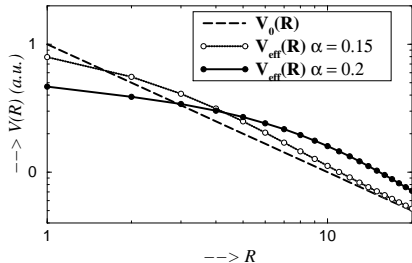

FIG. 2. Effective Coulomb potential in a 1D system with $\alpha = 0$, $\alpha = 0.15$ and $\alpha = 0.2$ on a Log-Log scale. The dashed straight line represents the unscreened Coulomb interaction. Screening tends to flatten the effective potential at intermediate distances. The lattice spacing is taken to be unity.

In figure 3 the outcome of the continuum integral as a function of separation between the electrons is plotted. For clarity the proportionality constants are set to unity. The behavior for the 3D system is as expected: the polarization energy is negative and proportional to $1/|R|$. In the 1D system, however, the polarization energy is positive, implying that screening effects *increase* the repulsion between the charges. This explains the anti-screening of the Coulomb repulsion at large distances found in the exact calculation.
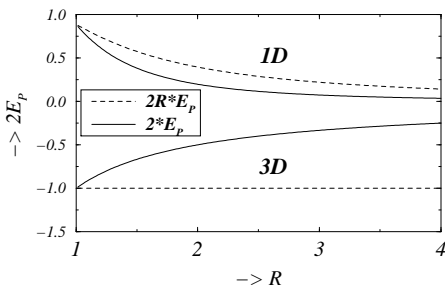

FIG. 3. The polarization energy $2E_p$ as a function of separation between the electrons in one and three dimensions in the continuum limit. The lattice spacing is taken to be unity and in the 1D system $r_0 = 0.5$.

The figure also shows that the polarization energy decays faster than $1/|R|$ at large distances. This can be expected since in 1 and 2D the integration is not over a volume, but rather over a line and a surface respectively. The consequence is that in low dimensional systems the

Coulomb potential is unscreened at large distances.

The exact calculation for the 1D system shows that the screening energy is negative at short distances. This can be understood by considering the limiting case where the two charges are on the same atom. The polarization energy associated with a single electron is a constant times the square of its electrical field $-cF^2$, so that the total polarization energy of a system where two electrons are infinitely far apart is $-2cF^2$. If the two electrons are on the same site, the total field is $2F$ resulting in a polarization energy of $-4cF^2$. So the screening energy related two charges at the same site is always more negative than the screening energy of two charges far apart, explaining why at short distances the Coulomb potential is always screened.
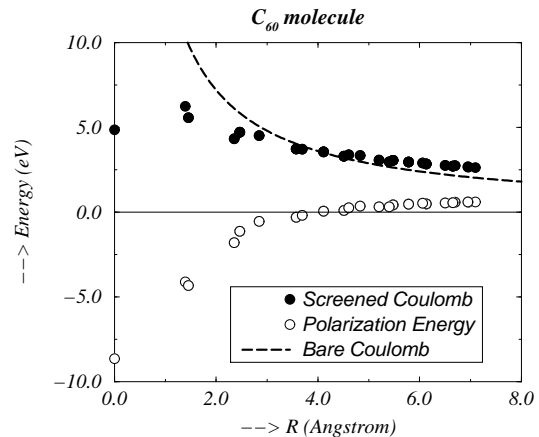

FIG. 4. The effective Coulomb interaction as function of the separation of two electrons on a C_{60} molecule. The carbon-carbon distance is 1.391 & 1.455 Å and the carbon polarizability is taken to be 0.56 Å^3

We now turn to a few finite size systems. For a C_{60} molecule we can model the screening by assuming that on each carbon site a dipole moment can be induced due to two excess charges on the molecule. The effective Coulomb repulsion between these two charges is calculated by the method described above. The results for the C_{60} molecule is shown in figure 4. Whereas the bare Coulomb repulsion depends strongly on the distance between the charges (ranging from $\sim$13.5 to $\sim$2 eV), screening tends to flatten the effective interaction (ranging from $\sim$6 to $\sim$3 eV). This is again due to the fact that at short distances the Coulomb interaction is screened and at large distances anti-screened, as in the 1D case. This behavior compares well with what has been found by Gunnarsson *et al* [9] and Lof *et al* [10].

In figure 5 the results for benzene and two linear benzologues, naphthalene and an polymer consisting of 200 benzene rings, is shown. The carbon-carbon distances and carbon polarizability are taken from reference [11]. The Coulomb potential for larger molecules is screened more effectively because more atoms participate in the

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screening process. For all these systems, however, the variation of the effective Coulomb potential over the molecule is drastically reduced by screening effects. For distant neighbors there is anti-screening, since the introduction of an electron on the molecules moves screening charge to the opposite site of the molecule causing the screening clouds of the two charges to interfere destructively. Obviously this makes the C_{60} molecule and the linear benzologues less correlated: the electrons move in a relatively uniform effective potential. Interesting also is that the on-site and nearest neighbor Coulomb interactions in these systems are almost equal, which really makes a Hubbard-like description very questionable. This explains why one-particle theories that do not take correlation effects fully into account, work so well for large organic molecules.
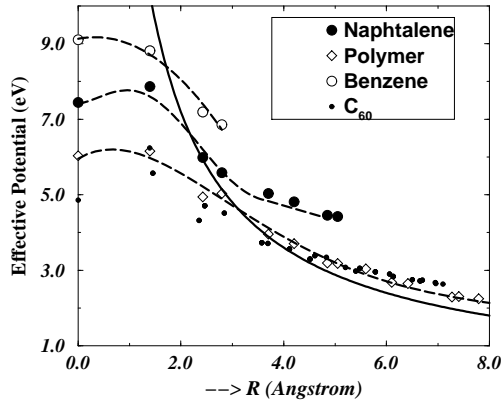

FIG. 5. The effective Coulomb interaction on different organic molecules. The carbon polarizability is 0.56 Å^3. The full line represents the bare Coulomb repulsion. The dashed lines are guides for the eye.

We considered, in conclusion, a point-dipole model to account for the screening of the Coulomb repulsion in non-polar insulators. For three dimensional systems the deviations from the Clausius-Mossotti result for the intersite screened Coulomb interaction are small, but in one and two dimensional systems only local field effects contribute to the screening. At large distances the Coulomb interaction is unscreened and in 1D at intermediate distances the Coulomb interaction is even anti-screened. Applying the dipole screening model to finite size systems like large organic molecules, we showed that the effective Coulomb interaction is only weakly dependent on the distance between the electrons. So correlation effects are drastically reduced, explaining the success of, one-particle, molecular orbital theory for large molecules.

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